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CLAIMS

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[Claim(s)]

[Claim 1] It comes to have a metallic-oxide transparent electrode layer on a thermoplastics substrate. This thermoplastics substrate The transparent-electrode plate for organic EL devices characterized by satisfying (\*\*) of the following - (Ha) requirements: (b) JIS The ten-point average of roughness height Rz by B0601 4nm or less, and the maximum difference of elevation Ry -- 20nm or less -- coming out -- a certain surface surface smoothness and (\*\*) -- the saturation water absorption (JIS K7209) by the Karl Fischer technique (JIS K0068) 0.02 or less % of the weight JIS of the thermoplastics which comes out and constitutes a certain low absorptivity and (Ha) a substrate Difference  $\Delta T (= T_{mg} - T_{wp})$  of the midpoint glass transition temperature  $T_{mg}$  by K7121 and the endoergic peak temperature  $T_{wp}$  accompanying water absorption isolation is  $20 \text{ degree-C} < \Delta T < 100 \text{ degree C}$ .

[Claim 2] The thermoplastics which constitutes a substrate is JIS. Transparent electrode plate according to claim 1 whose latent heat accompanying the crystal fusion by K7122 is a non-crystalline polymer 2.1J [ /g ] or less.

[Claim 3] The thermoplastics which constitutes a substrate is a transparent electrode plate according to claim 1 or 2 which is an annular olefin system polymer.

[Claim 4] The organic EL device with which it has the laminated structure which allotted the organic luminous layer, and this transparent electrode plate consists of a transparent electrode plate according to claim 1 to 3 between the two electrodes which consist of a transparent electrode plate and a back plate.

[Claim 5] Furthermore, the organic EL device of claim 4 which comes to carry out the laminating of a hygroscopic resin layer and the dampproof film layer.

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[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the organic EL device containing the transparent electrode plate which constitutes one [ which electric field are impressed / one / and makes it emit light in the organic luminescence (ingredient) layer pinched by the electrode plate of a couple / at least ] electrode plate of an organic EL device ("electroluminescence" is written as "EL" according to a common name), and this transparent electrode plate.

[0002] The application as the back light for liquid crystal display components (source of a fill-in flash), a night-light, a road sign, a night announcement, etc. is expanding an organic EL device as a component of the self-luminescence mold excellent in a light weight and mechanical endurance, and also, in development of each color luminescence organic material, the development as a thin shape, a high angle of visibility, high-speed responsibility, and a high definition (full color) display device is progressing conjointly.

[0003] The transparent electrode plate which while constitutes a luminescence (display) side side at least among the electrode plates of the couple which pinches the organic luminous layer of such an organic EL device, and formed the metallic-oxide transparent electrode layer represented with the tin dope indium oxide film (henceforth the "ITO film" according to a common name) on the transparence substrate as an electrode plate is used.

[0004] In a transparence substrate, at transparency In addition, the thing which the heat-resistant and flat transparent electrode layer for forming a metallic-oxide transparent electrode layer by vacuum evaporation on it is formed, and a transparent electrode layer exfoliates leakage current and under an activity more nearly locally than a substrate, Or in order to prevent the degradation by the phenomenon peculiar to an organic EL device of generating of the dark spot (nonluminescent section) understood as causes with main local poor vacuum evaporation taking place with surface irregularity, To have the flat side of the degree of pole by itself is needed (for example, JP,11-126689,A). For this reason, although the glass substrate which fulfills such demand characteristics good has been conventionally used as a transparence substrate, in order to aim at much more improvement the lightweight nature of an organic EL device, shock-proof, or flexible, the activity of a transparence resin substrate is also considered. as a transparence resin substrate, the substrate which consists of thermoplastics, such as polyethylene terephthalate, a polycarbonate, polyether sulphone, a polyether ether ketone, and polypropylene, is also proposed -- \*\*\*\* (JP,2-251429,A) -- these thermoplastics has a difficulty in respect of thermal resistance and surface surface smoothness, and the activity of the thermosetting resin substrate which was cautious of surface surface smoothness with precision casting etc., and was formed is made desirable (JP,9-129376,A).

[0005]

[Problem(s) to be Solved by the Invention] According to research of this invention persons, however, the thermosetting resin substrate by the precision casting method The surface surface smoothness of the degree of pole required of the transparence substrate of an organic EL device is not filled (the maximum

surface roughness recommended by above-mentioned JP,11-126689,A receives 10nm or less). The number of projections more than 600A (60nm) which exists in the field of 500-micrometer angle according to the example 1 of above-mentioned JP,9-129376,A is made into 15 pieces. When an ITO electrode layer was formed on it, the degradation by the above-mentioned generating of a dark spot was not avoided (the example of comparison 1 below-mentioned reference).

[0006] The main objects of this invention are by preventing the degradation of the organic EL device by generating of a dark spot etc. with the transparent electrode plate which used the transparence resin substrate to offer a reliable organic EL device.

[0007]

[Means for Solving the Problem] And it is characterized by for the transparent electrode plate for organic EL devices of this invention developed in order to attain the above-mentioned object coming to have a metallic-oxide transparent electrode layer on a thermoplastics substrate, and this thermoplastics substrate satisfying following (\*\*) - (Ha) requirements.

[0008] (b) JIS The ten-point average of roughness height Rz by B0601 4nm or less, And 20nm or less, the maximum difference of elevation Ry comes out, and is a certain surface surface smoothness and (b) JIS. The saturation water absorption by K0068 0.02 or less % of the weight, JIS of the thermoplastics which comes out and constitutes a certain low absorptivity and (Ha) a substrate Difference  $\Delta T$  (=  $T_{mg} - T_{wp}$ ) of the midpoint glass transition temperature  $T_{mg}$  by K7121 and the endoergic peak temperature  $T_{wp}$  accompanying water absorption isolation is  $20\text{ degree-C} < \Delta T < 100\text{ degree C}$ .

[0009] Moreover, the organic EL device of this invention is characterized by having the laminated structure which allotted the organic luminous layer, and this transparent electrode plate consisting of the above-mentioned transparent electrode plate between the electrode plates which consist of a transparent electrode plate and a back plate.

[0010] this invention persons inquire for the above-mentioned object, and add a little about the circumstances which reached this invention.

[0011] In the organic EL device obtained using the transparent electrode plate which the thermosetting resin substrate formed by the casting method does not fill the surface surface smoothness required of the substrate of the transparent electrode plate for organic EL devices as described above, and formed the metallic-oxide transparent electrode layer on it, and was obtained, generating prevention of a dark spot is difficult (the below-mentioned example 1 of a comparison). Lowering of such surface surface smoothness is an unescapable fault accompanying being for producing a hollow minute on a front face in case resin depolymerizes, a monomer and oligomer generate and this is desorbed from a front face, a crack, climax, etc. a part, and using thermosetting resin as a substrate ingredient rather on the occasion of hardening by the UV irradiation and heating of thermosetting resin which carried out casting. On the other hand, as for the thermoplastics sheet which has the surface surface smoothness of the substrate of extent required of formation of an organic EL device, according to this invention persons' knowledge, marketing has also already been carried out by controlling extrusion-molding conditions etc. to a precision (for example, polyethylenenaphthalate film used in the below-mentioned example 4 of a comparison). However, according to research of this invention persons, by having only used as a substrate the thermoplastics sheet which has such good surface surface smoothness, degradation, such as generating of the brightness nonuniformity peculiar to an organic EL device by a dark spot etc., is not avoided. As a result of this invention person's etc. inquiring wholeheartedly, it has been solved using a transparence resin substrate that the first stage surface surface smoothness of the transparence resin substrate used for generating of the dark spot generated when a transparent electrode plate is formed also has effect with important absorptivity of the resin used with last thing and water absorption isolation property under heating. It faces forming metallic-oxide transparent electrode layers, such as ITO, on a transparence resin substrate, and is washing of a substrate. - It dries. - Processes, such as patterning-washing-desiccation by vacuum evaporation formation-etching of metallic-oxide transparent electrode layers, such as ITO, are included, and substrate resin goes via the process of absorption-stoving of the solvent which makes water (pure) representation thru/or a washing medium unescapable. Especially on the occasion of stoving, if there are many absorbed water parts, the bleedoff gives quite rapid stress to a

resin substrate front face and the transparent electrode layer on it, and deformation of the substrate front face connected with interfacial peeling of a subsequent transparent electrode layer or generating of a crack, and the partial exfoliation with the direct transparent electrode layer after vacuum evaporation may take place further: moreover -- even if water absorption moisture passes through a desiccation process -- the inside of the transparent electrode plate in a product organic EL device -- some -- remaining -- transparent electrode formation long-term in use -- public funds -- rather than it is based on the corrosion of a group oxide -- the volume -- size -- hydroxide-ization is caused and it leads to generating of swelling of an electrode layer, a crack, etc. therefore, in order for the dark spot in an organic EL device to carry out generating prevention also including the formation process of a metallic-oxide transparent electrode layer, this invention persons While having very small absorptivity (b) as resin to be used The resin which has the glass transition temperature (Ha) appropriately set up by relation with the endoergic peak temperature accompanying water absorption isolation with the heating conditions in a metallic-oxide transparent electrode layer is selected. And it is required to form the resin sheet thru/or film which has good surface surface smoothness (b) as much as possible by controlling manufacture conditions using selected resin. Using a thermoplastics substrate rather for that purpose carries out the knowledge of the desirable thing, and it reaches this invention.

[0012]

[Embodiment of the Invention] Drawing 1 and 2 are type section drawings of the organic EL device which has the comparatively easy configuration which starts one example of this invention, respectively.

[0013] With reference to drawing 1, the organic EL device concerning this example comes further to carry out the laminating of the dampproof films 4 and 4 of a couple to the both sides of the laminating structure which comes to pinch the organic luminous layer 1 with the electrode plate of a couple which consists of the transparent electrode plate 2 and back plate 3 by the side of the screen. According to this invention, the transparent electrode plate 2 by the side of the screen comes to form metallic-oxide transparent electrode layer 2b on thermoplastics substrate 2a, and the back plate 3 which is from a metallic oxide or a metal on the reverse side of the transparent electrode plate 2 further as an electrode which counters is formed. The laminated structure containing the transparent electrode layer 2 and a back plate 3 is closed by the laminating of other damp proof courses 5 (drawing 2) which consists of a layer 4 or a metallic oxide of a dampproof film etc. further. The lead wire connected to a power source 6 (a direct current or alternating current) is attached, and the transparent electrode plate 2 and the back plate 3 are made into the structure which can impress an electrical potential difference to the organic luminous layer 1 here.

[0014] transparence substrate 2a which constitutes the transparent electrode plate 2 by the side of the screen according to this invention -- following requirements (\*\*) -- it is the thermoplastics substrate which fills - (Ha). (In addition, a back plate 3 is a metaled monolayer or a metaled double layer electrode, or may be the laminated material of the transparent electrode layer of a metal or a metallic oxide, and the substrate which is not transparent.) Either can be chosen if needed.

(b) JIS The ten-point average of roughness height Rz by B0601 4nm or less, And 20nm or less, the maximum difference of elevation Ry comes out, and is a certain surface surface smoothness and (b) JIS. The saturation water absorption by K0068 0.02 or less % of the weight, JIS of the thermoplastics which comes out and constitutes a certain low absorptivity and (Ha) a substrate Difference  $\Delta T (= T_{mg} - T_{wp})$  of the midpoint glass transition temperature  $T_{mg}$  by K7121 and the endoergic peak temperature  $T_{wp}$  accompanying water absorption isolation is 20 degree-C <  $\Delta T$  < 100 degree C.

[0015] following and requirements (\*\*) - (Ha) is explained serially.

[0016] (b) Surface surface smoothness thermoplastics substrate 2a is JIS. Preferably, the 20nm or less of the 10nm or less of the 2nm or less; maximum differences of elevation Ry comes out preferably, and the ten-point average of roughness height Rz by B0601 (criteria die length: 0.08mm, assessment die length of 0.04mm) uses 4nm or less of a certain things. Specifically, Rz in this description and Ry value are based on the measured value in the ordinary temperature by the atomic force microscope (product made from SEIKO Electron "SPI3800/SPA300HV"), and ordinary pressure.

[0017] If the comparatively bad thermoplastics substrate of surface smoothness is used, since  $R_z$  exceeds 4nm or it has the granularity to which  $R_y$  exceeds 20nm, namely, generating of a dark spot will increase and the luminescence brightness as an organic EL device will become small, it becomes unsuitable as goods.

[0018] Although there is especially no limit, generally it is selectable, if thermoplastics substrate 2a is the thickness suitable for production of an EL element suitably from the range of about 5-300 micrometers in consideration of reinforcement, flexibility, etc. The area is determined by a required display thru/or luminescence area, and although there are many 20mm - about 2000mm things as diagonal die length, component development of a large area is also expected more by amelioration of the organic material which constitutes the organic luminous layer 1. From the substrate sheet of the area which generally becomes size more, the substrate sheet of area required for a component is cut suitably, and is prepared.

[0019] the above thermoplastics sheets of thickness -- general -- solution casting (casting) -- law and a melting extrusion method, although formed more of cutting from a heavy-gage moldings etc. Surface roughening with which the maximum difference of elevation  $R_y$  calls cutting 100-5000nm from a limit of machining precision is not avoided again by evaporation of the solvent which uses the solution casting method, and surface smooth nature which is said very much to \*\*\*\* as  $R_z \leq 4\text{nm}$  and  $R_y \leq 20\text{nm}$  is not expectable. It is desirable to use a melting extrusion method for obtaining this surface surface smoothness. That is, heating fusion of the resin is carried out with a monopodium or a biaxial extruder, and, subsequently this melting resin is led to flat dies, such as a T die or a coat hanger die, through a conduit, and from the lip section of this flat die, the melting resin of the shape of the shape of a sheet and a film is made to breathe out, and it pulls out. The front face of the cast roll which comes to carry out temperature management is contacted, it is cooled, and this pulled-out melting resin serves as the solidified sheet or film. At this time, it is desirable to use as a substrate the thermoplastics sheet or films by the melting extrusion method which comes to control conditions to a precision of the rate of the temperature of melting resin, discharge quantity distribution of the melting resin of the cross direction of said die, and a cast roll and temperature, and the front face of a cast roll and melting resin, such as adhesion. Since it excels in the below-mentioned nonhygroscopic (\*\*) in this viewpoint and that pyrolysis temperature and melting extrusion temperature approximate PCTFE (polychlorotrifluoroethylene resin) which is the ingredient of the typical dampproof films 4 and 5, shaping by the melting extrusion method is difficult, and since it cannot but depend for film shaping on the solution casting method or a cutting method, as a transparence substrate ingredient used for a transparent electrode plate, it is unsuitable.

[0020] (b) Low absorptivity thermoplastics substrate 2a is JIS. The saturation water absorption (JIS K7209) by K0068 (curl Fischer coulometric titration) uses 0.02 or less % of the weight of a thing. Measurement is faced and it is JIS. The test piece which cut down the measuring object film thru/or the sheet for the square whose one side is 50mm based on K7209 It dries for 24 hours in the thermostat kept at 50 degrees C. In a desiccator After radiationnal cooling, In the pure water maintained at the temperature of  $23 \pm 2$  degrees C, after 170-hour (it extends from 24 hours of JIS criteria) neglect, Through flow drying of the test piece is carried out for 10 minutes at ejection and 60 degrees C, except for the attached groundwater on the front face of a sample, after that, a moisture content is titrated with curl Fischer coulometric titration (JIS K0068), and saturation water absorption is searched for. The numeric value of a publication in this description is based on the measured value by the coulometric-titration type water measurement equipment "CA-06 mold" by Mitsubishi Kasei Corp.

[0021] If the saturation water absorption of thermoplastics substrate 2a to be used exceeds 0.02 % of the weight, as it probably \*\*\*\*\* (ed), it will absorb water by contact to the drainage system medium in the inside of the formation process of transparent electrode layer 2b, and control of a dark spot will become difficult through the moisture residue to the inside of the adverse effect at the time of the moisture bleedoff by subsequent desiccation, and the electrode plate in a manufacture organic EL device etc. Surface surface smoothness and item (Há) fitness glass transition temperature, simultaneously the polyethylene terephthalate (saturation water absorption = 0.128 % of the weight) that needs to be filled

have greatly unsuitable saturation water absorption. the demand characteristics of the substrate which described this property previously -- setting -- item (\*\*) -- Saturation water absorption of polyethylenephthalate (saturation water absorption = 0.209 % of the weight) is greatly unsuitable. Although saturation water absorption is small, surface surface smoothness (ten-point average-of-roughness-height  $R_z = 120\text{nm}$ , maximum difference-of-elevation  $R_y = 400\text{nm}$ ) of polypropylene (saturation water absorption = 0.010 % of the weight) is [ water absorption ] greatly unsuitable. As for saturation water absorption, it is desirable that they are especially 0.01 or less % of the weight and 0.005 more % of the weight or less.

[0022] (c) Fitness glass-transition-temperature thermoplastics substrate 2a is JIS of the thermoplastics which constitutes this. Difference  $\Delta T (= T_{mg} - T_{wp})$  of the midpoint glass transition temperature  $T_{mg}$  by K7121 and the endoergic peak temperature  $T_{wp}$  accompanying water absorption isolation needs to fill the relation which is  $20\text{ degree-C} < \Delta T < 100\text{ degree C}$ . The midpoint glass transition temperature  $T_{mg}$  (JIS K7121) shows the temperature of the intersection of both the base lines, the intermediate cable drawn at the equal distance, and a DSC curve based on the base line before and behind the transition process in the DSC (differential scanning calorimetry) curve for programming-rate/of 10 degrees C. Moreover, the endoergic peak temperature  $T_{wp}$  accompanying water absorption isolation was searched for according to the crystal fusion peak thermometry on the DSC curve for programming-rate/of 10 degrees C by the heat-of-transition measuring method set to JISK7121, however says the endoergic peak temperature in the about 60-90-degree C temperature requirement accompanying balking as free water of water absorption (moisture which is probably in \*\*\*\*\*).

[0023] If shocking change of a water absorption condition [ in / that this temperature-gradient  $\Delta T (= T_{mg} - T_{wp})$  is 100 degrees C or more / a desiccation process ] is added, it will become difficult for a brittle crack to become easy to go into a substrate, to produce the nonluminescent section by the dark spot in a luminescence side in the long-term activity of a product organic EL device, and to maintain early brightness. On the other hand, dehydration time amount [ in / that this temperature-gradient  $\Delta T$  is 20 degrees C or less / a desiccation process ] becomes long, and it is not not only desirable on a production process, but it may produce degradation of an up metallic-oxide transparent electrode layer for the residual moisture to a substrate top. Acrylic thermosetting resin ( $\Delta T = 12\text{ degree C}$ , example 1 of the below-mentioned comparison) is not desirable in this viewpoint, either. Moreover, as thermoplastics which is not desirable, there are polystyrene, polyethylene terephthalate, rigid PVC, etc. in this viewpoint.

[0024] (d) moreover, the thermoplastics which constitutes substrate 2a -- JIS K7122 -- being based -- DSC with a programming rate of 10 degrees C -- it is desirable that the latent heat (it is comparison proofreading by the heat of fusion and the indium standard sample) measured by law shows the substantial amorphism of 2.1 or less J/g. When the crystallinity to which the latent heat exceeds g in 2.1J /is shown, if it not only becomes easy to carry out surface roughening according to generating of a spherulite, but shocking change of a water absorption condition is added in a desiccation process by the cooling process of a melting extrusion resin sheet, it will become easy to produce the micro crack which leads to generating of a dark spot by the volume change.

[0025] The graph which shows the example of a type of the endoergic behavior in the temperature-up process by DSC about a thermoplastics substrate for an understanding of the above-mentioned property (Ha) and (d) is shown in drawing 6.

[0026] The ease which gives the demand characteristics of above-mentioned (b) - (d) is taken into consideration. As thermoplastics substrate 2a An annular olefin system polymer (for example, thing indicated by JP,11-216817,A or JP,8-142263,A), While considering polycarbonate resin, polyester polycarbonate resin, etc. about a presentation, molecular weight, etc. that property (b) - (d), and an extrusion property should be satisfied and choosing resin The temperature of the melting resin described previously that item (b) surface surface smoothness should be satisfied, discharge quantity distribution of the melting resin of the cross direction of a flat die, It is desirable to use a 10-200-micrometer sheet thru/or a film preferably 5-300 micrometers in thickness obtained by T-die melting extrusion method on the conditions which controlled the adhesion of the rate of a cast roll and temperature, and the front face

of a cast roll and melting resin etc. to the precision. It is desirable to use the melting extrusion sheet thru/or film of an annular olefin system copolymer with which saturation water absorption consists of less than [ about 0.001 % of the weight or it ], a very small annular olefin system polymer especially a copolymer of an alpha olefin (ethylene is included) and an annular olefin, a copolymer of the annular olefin monomer which does not give a norbornane ring, and the annular olefin monomer which gives a norbornane ring, etc. especially and which has improved amorphism nature and a melting extrusion property more.

[0027] After passing through pretreatment of washing-desiccation according thermoplastics substrate 2a obtained as mentioned above to media, such as an acetone and pure water, etc. if needed, the transparent electrode plate (2) of this invention is obtained when thickness forms preferably 1-200nm of metallic-oxide transparent electrode layer 2bs of about 5-100nm in the whole surface by RF sputtering, DC sputtering, ECR (electron cyclotron resonance) plasma sputtering, vacuum deposition, ion plating, etc.

[0028] As a metallic oxide which constitutes transparent electrode layer 2b, although ZnO, SnO<sub>2</sub>, and In<sub>2</sub>O<sub>3</sub> grade are used, IZO (zinc dope indium oxide), ITO (tin dope indium oxide), etc. are more desirable, and the ITO film which doped about 5 - 15% of the weight of SnO<sub>2</sub> more preferably one to 50% of the weight to indium oxide especially is used preferably. Metal oxide layer 2b after membrane formation is patternized through after treatment, such as patterning (etching)-resist clearance-(water) washing-desiccation by the etching gas of etching reagents, such as dilute acids, such as ion for grain adjustment or heat-treatment, and dilute hydrochloric acid, or iodic-acid-ferri-chloride mixture, or HBr, C<sub>2</sub>H<sub>2</sub>, Cl<sub>2</sub>, SF<sub>6</sub> and CF<sub>4</sub>, or CHF<sub>3</sub> grade, if needed. Thus, although the transparent electrode plate 2 which has transparent electrode layer 2b before the transparent electrode plate 2 which has metallic-oxide transparent electrode layer 2b by which patterning was carried out, and patterning can all be set as the object of a negotiation as a product, it can also go into the production process of the organic EL device which continues, of course continuously.

[0029] Although you may be the two-layer structure object 2 which formed metallic-oxide transparent electrode layer 2b in the whole surface of thermoplastics substrate 2a as the transparent electrode plate of this invention is contained in the example of the organic EL device of drawing 1 mentioned above and drawing 2 and is taken out and shown in drawing 3, it can also consider as the laminated structure which inserted adhesives layer 2c between thermoplastics substrate 2a and transparent electrode layer 2b, and has improved the adhesion of transparent electrode layer 2b as shown in drawing 4 if needed.

[0030] As adhesives which constitute adhesives layer 2c, the silane coupling agent which introduced an urethane system, a polyester system, acrylic, a hydrolysis nature machine, and organic functional groups (an alkoxy group, an acetoxyl radical, halogen, etc.) (the amino group, an methacrylic radical, a vinyl group, an epoxy group, sulfhydryl group, etc.) may be used. Moreover, corona treatment may be beforehand performed to the electrode stratification side of a thermoplastic substrate in the range which does not check front-face nature. such adhesives layer 2c -- close -- the above-mentioned (\*\*) -- the improvement effectiveness in dependability of the organic EL device which led generating prevention of the dark spot by using - (Ha) and thermoplastics substrate 2a which satisfies the property of (d) further etc. is not spoiled substantially

[0031] Moreover, in order to improve further the endurance of the organic EL device obtained eventually, it is also desirable to prepare 2d of damp proof courses in an EL element forming face side, a reverse side (for it to illustrate as drawing 5), or its both sides the EL element forming face side of substrate 2a, and to decrease attainment of the moisture to the organic luminous layer 1 as much as possible to the transparent electrode plate of this invention. Although the ingredient of the arbitration which can prevent transparency of moisture with a thin film is used as 2d of damp proof courses, it is usually formed from the independent or compound film. [ of a metal and metallic compounds ] For example, a kind of metallic oxides, such as metal simple substances, such as aluminum, titanium, chromium, and nickel, an aluminum oxide, oxidization silicon, titanium oxide, a ferrite, the silver oxide, chromic oxide, antimony oxide, a zinc oxide, molybdenum oxide, cobalt oxide, a zirconium dioxide, tungstic oxide, oxidization copper, nickel oxide, oxidization vanadium, oxidization MAGUSHIUMU, manganese oxide, lanthanum oxide, a lead oxide, oxidization KADONIUMU, and bisumuth oxide, or



these metals, and metallic compounds or two sorts or more of combination is used. It is oxidation silicon especially preferably. The formation approach has vacuum evaporation and a common sputter. Thickness is 50-500nm, and since transparency and coloring will become large if it becomes thick with dampproofing, it selects thickness in the range which does not check the luminescence engine performance of an EL element. Moreover, as 2d of damp proof courses, it is a simple substance about moisture-proof film, such as said metal, a metallic oxide, or metallic compounds, or the laminating of the film of resin can be carried out to the front face, and it can be used for it. Although there is especially no limit, as this resin Polyethylene terephthalate, Polybutylene terephthalate, polyethylenenaphthalate, a polycarbonate, Cycloolefin system resin, polyethylene, polypropylene, styrene resin, A polyamide, polyvinyl alcohol, a polyvinyl acetate copolymer, polyurethane, Polyphenylene SURUFIDDO, a polyether ether ketone, polyimide, Polyether SURUFIDDO, a polyoxyethylene, vinyl chloride resin, Two or more kinds of mixture of fluorine system resin, such as vinylidene-chloride system resin, polyvinyl fluoride, fluorination vinylidene resin, and an ethylene 4 fluorination ethylene copolymer, an acrylic-acid system copolymer, a methacrylic-acid system copolymer, a urea resin, and also these resin can be chosen suitably.

[0032] 2d of damp proof courses may be the laminating structure, and they are a simple substance about said metal or metallic oxide etc., or may carry out the laminating of the film of resin to the front face. Especially the structure that pinches the layer of hygroscopic resin, such as polyvinyl alcohol, between the layers of this film is desirable.

[0033] Moreover, in order to give weatherability and antifouling property, the resin layer which consists of simple substances of resin, such as fluorine system resin, such as fluorination vinylidene resin, polyvinyl fluoride, tetrafluoroethylene resin, and an ethylene 4 fluorination ethylene copolymer, an acrylic-acid system copolymer and a methacrylic-acid system copolymer, polyethylene terephthalate, and a vinyl chloride, or two or more kinds of those mixture may be prepared in the outside of this electrode surface, or the outside of 2d of damp proof courses.

[0034] Moreover, these resin may also contain an ultraviolet ray absorbent, an ultraviolet-rays electric shielding agent, light stabilizer, a pigment, a color, and an extending agent if needed 0.1 % of the weight to 30% of the weight.

[0035] Although there is no thickness of the layer of these resin, it sets especially a limit to 5 micrometers - 200 micrometers in many cases.

[0036] A back plate 3 is good also as equivalent as substantially as the configuration of the transparent electrode plate 2 by the side of the screen, or good also as the monolayer by the metaled electrode, or a laminating configuration.

[0037] The configuration of the organic luminous layer 1 does not differ especially from the thing especially contained in the conventional organic EL device. Namely, various coloring matter, such as metal complexes, such as a quinolinol derivative, a styryl benzenoid compound, a JISUCHIRIRU pyrazine derivative, a polyphenyl compound, the North America Free Trade Agreement RUIMIDO derivative, a perylene derivative, and an OKISA diazole derivative; it can also consider as the independent layer of organic luminescent material, such as fluorescent brightener [, such as a benzothiazole system benzimidazole, and benzooxazole, ], or the multilayer structure which accepted to the electron hole transporting bed at the anode plate side, accepted the need in the electronic injection layer additionally at the cathode side, and was established. The organic luminous layer 1 is formed in the thickness of the range of 5nm - 5000nm as a whole by such a monolayer or multilayer structure.

[0038] The organic EL device of drawing 1 is obtained by closing the laminated structure which comes to \*\* such an organic luminous layer 1 with the electrode plates 2 and 3 of a couple between the dampproof film 4 of a couple, and 4.

[0039] As dampproof films 4 and 4, a PCTFE (polychlorotrifluoroethylene resin) film is used, and also a laminating (alternation) multilayer (PCT/JP's 98/01781 and Japanese Patent Application No. No. 127437 [ 11 to ]) with a hygroscopic or non-hygroscopic resin layer, an inorganic oxide, or the metaled vacuum evaporation film is used suitably. In many cases, the 30-1000 micrometers especially of these whole multilayer moisture-proof film thickness are about 50-500 micrometers.



[0040] In the organic EL device of drawing 2, one side by the side of the tooth back of the dampproof films 4 and 4' of the couple in the example of drawing 1 It is transposed to other dampproof layers 5 which consist of a metal oxide layer which constitutes the 2d ( drawing 5 ) of the above-mentioned damp proof courses. In the outside of the electrode plate 2 and a back plate 3 By forming the hygroscopic resin layer (water-capturing layer) 7, respectively, catching the water of few amounts which may penetrate the dampproof film 4 thru/or the dampproof layer 5, and controlling transparency of the moisture to the organic luminous layer 1 Lowering of the life by degradation of the organic material which constitutes the organic luminous layer 1 is controlled. The other configuration is the same as it of drawing 1.

[0041] The hygroscopic resin layer 7 is formed as a layer with a thickness of about 5-200 micrometers with hygroscopic resin, such as polyvinyl alcohol (partial saponification polyvinyl acetate) and nylon.

[0042] in addition, trespass of the moisture from the side of a component -- nearby -- in order to prevent effectively -- the dampproof layer 5 -- changing -- or -- in addition, the hardened material of the epoxy resin (layer) extended from a component rear face to the side or acrylic ultraviolet-rays hardening resin (layer) may be prepared.

[0043]

[Example] Hereafter, an example and the example of a comparison explain this invention still more concretely.

[0044] (Example 1) COC resin was fused using annular olefine resin (it abbreviates to "COC resin" "ZEONOA" by Nippon Zeon Co., Ltd., and the following) with the shaft diameter of 50mm set as 260 degrees C, and the single screw extruder of ratio-of-length-to-diameter=26. Subsequently, it led to the T die with a die lip width of face of 700mm set as 260 degrees C via the conduit, and the melting regurgitation was carried out from the die lip. Subsequently, it was the cast roll set as the skin temperature of 150 degrees C, and taking over at uniform velocity, made homogeneity contact, it was made to solidify and the film with a thickness of 50 micrometers was obtained. The organic EL device of lamination shown in general in drawing 2 was formed using this film as substrate 2a. However, in this organic EL device, transparent electrode 2b and a back plate 3 are made into the shape of a rectangular stripe, and the water trapping nature resin layer 7 by the side of a back plate 3 is not formed.

[0045] This COC resin substrate showed the surface surface smoothness whose ten-point average of roughness height Rz is 1.5nm and whose maximum difference of elevation Ry is 4.0nm by the surface roughness test (JIS B0601) performed by ordinary temperature/ordinary pressure using the atomic force microscope. Moreover, the saturation water absorption (170-hour immersion among JIS K7209 and 23-degree C distilled water) by the Karl Fischer technique (JISK0068) showed 0.001 % of the weight and very good low hygroscopicity, and checked that midpoint glass-transition-temperature Tmg=166 degree C, endoergic peak temperature Twp=73 degree C accompanying water absorption isolation,  $\Delta T = T_{mg} - T_{wp} = 93$  degree C, and the crystal heat of fusion were less than 2.1 J/g by DSC measurement by part for programming-rate/of 10 degrees C.

[0046] Following process (i) - (x) was serially given to the above-mentioned COC resin substrate of an about 8cmx8cm angle, and the organic EL device was formed.

[0047] (i) The acetone washed at the room temperature, subsequently pure water washed the above-mentioned resin substrate for 180 seconds with the acetone further for 180 seconds for 180 seconds first, and it dried for about 60 seconds at 90 degrees C with (ii) far-infrared dryer. (iii) Subsequently to in commercial DC magnetron sputtering system, the substrate was installed, the inside of a vacuum tub was decompressed below to  $1 \times 10^{-3}$  Pa, it held for 10 minutes at 90 degrees C with substrate temperature, and the substrate was dried further. (iv) The ITO film with a thickness of 200nm was formed in the whole surface of a substrate for transparent electrodes by DC magnetron sputtering after that. (v) Subsequently to an ITO film top, a photoresist ("OFPR" by TOKYO OHKA KOGYO) is applied. Alignment exposure is carried out through the photo mask made from quartz glass (TOKYO OHKA KOGYO make). Development with exclusive developed image liquid (TOKYO OHKA KOGYO make), etching by 10% hydrochloric-acid underwater ordinary temperature immersion, Stoving of the substrate which formed ten stripe-like ITO electrodes by line breadth [ of 5mm ] and pitch 8mm was

carried out for 120 seconds at 90 degrees C with far-infrared heating apparatus through the process which washes for 180 seconds with pure water further, and is washed for 180 seconds with an acetone after deeded resist clearance. (vi) Next, this substrate was fixed to the substrate electrode holder of a vacuum evaporator, the inside of a tub was decompressed to  $1 \times 10^{-4}$  or less Pa, the substrate was heated at 90 degrees C, and it held for 10 minutes. (vii) The luminous layer of the organic electroluminescence which consists of an aluminum complex which makes a kino reel derivative a ligand was produced by vacuum evaporatio in thickness of 50nm after that. Subsequently to a sputtering system, a substrate is moved. To an aluminum plate with a thickness of 1mm at a place with an organic electroluminescence emitter side-face right above spacing of 0.2mm Width of face of 5mm, (viii) Install the metal mask which has ten band-like space with a spacing of 3mm so that it may intersect perpendicularly with the pattern of an ITO electrode, and a Mg-Ag alloy is used as a target in DC spatter through this mask. The counterelectrode with a thickness of 200nm which intersects perpendicularly with the ITO film and consists of a width of face [ of 5mm ] and a spacing 3mm band-like counterelectrode pattern was formed. (ix) Next, after picking out lead wire from each electrode, with the sputtering system, on the Mg-Ag alloy electrode, the oxidation silicon film was produced in thickness of 200nm, and it considered as the damp proof course on the back. (x) Next, the two-layer film which comes to vapor-deposit an oxidation silicon layer with a thickness of 50nm with a vacuum deposition method to the film of polyethylene terephthalate with a thickness of 15 micrometers was formed, and the laminating was carried out on the resin substrate by the side of the screen of an EL element layered product. Furthermore, on it, the laminating of the moisture absorption film of the polyvinyl alcohol with a thickness of 30 micrometers dried with the 60-degree C vacuum dryer for 100 hours was carried out, and the laminating of the film of said oxidization silicon vacuum evaporatio polyethylene terephthalate was carried out further. The dry laminate method was used for each these laminatings approach. This formed the organic EL device of a 8cmx8cm angle.

[0048] Direct current voltage was applied between the counterelectrodes of the formed organic EL device, and 10mA /was made to emit light with the current density of 2 cm. When the initial luminescence condition was observed, the island-shape dark spot which does not emit light was not observed. Furthermore, continuation luminescence of this component was carried out in 60 degrees C and 90% of ambient atmosphere for 100 hours, and a subsequent dark spot and lowering of brightness were measured. Consequently, the maintenance factors of the dark spot of 3 per 3cmx3cm luminescence side field and brightness also including a non-picture element part were 85%.

[0049] (Example 2) as an activity resin substrate -- a front face -- the organic EL device was formed like the example 1 except using a polycarbonate resin sheet (the "pure ace" by Teijin, Ltd.) with a smooth thickness of 75 micrometers.

[0050] These substrates were midpoint glass-transition-temperature  $T_{mg}=152$  degree C, transition peak temperature  $T_{wp}=75$  degree C by water absorption, and latent-heat  $=2.1$  J/g average-of-roughness-height  $R_z=0.35$ nm, the 3.5nm of the maximum differences of elevation, and saturation water absorption  $=0.016\%$  of the weight as a result of the same measurement as an example 1.

[0051] Direct current voltage was applied to the created organic EL device, and light was made to emit with the current density of 10 mA/cm<sup>2</sup>. When the initial luminescence condition was observed, the island-shape dark spot which does not emit light was not observed. Furthermore, continuation luminescence of this component was carried out in 60 degrees C and 90% of ambient atmosphere for 100 hours, and a subsequent dark spot and lowering of brightness were measured. Consequently, the maintenance factor of the dark spot of five places and brightness was 78% in respect of luminescence of 3cm around.

[0052] (Example 1 of a comparison) As an activity resin substrate, the organic EL device was formed like the example 1 except using the sheet (ultraviolet-rays hardened material of acrylic-acid 2-cyano hexyl) of an acrylic resin hardened material with a thickness of 80 micrometers.

[0053] These substrates were midpoint glass-transition-temperature  $T_{mg}=85$  degree C, transition peak temperature  $T_{wp}=73$  degree C by water absorption, and latent-heat  $=8$  J/g average-of-roughness-height  $R_z=10$ nm, the 60nm of the maximum differences of elevation, and saturation water absorption  $=0.32\%$

of the weight as a result of the same measurement as an example 1.

[0054] Next, direct current voltage was applied to the organic EL device which carried out in this way and was created, and light was made to emit with the current density of 10 mA/cm<sup>2</sup>. When the initial luminescence condition was observed, 27 island-shape dark spots which do not emit light were observed for 3cm around. Furthermore, continuation luminescence of this component was carried out in 60 degrees C and 90% of ambient atmosphere for 100 hours, and a subsequent dark spot and lowering of brightness were measured. Consequently, luminescence was not seen for the dark spot at all breadth and 100 hours after in respect of luminescence of 3cm around on the whole surface.

[0055] (Example 2 of a comparison) As an activity resin substrate, formation of an organic EL device was tried like the example 1 except using polypropylene resin ("no-BUREN" by Sumitomo Chemical Co., Ltd.) with a thickness of 50 micrometers.

[0056] These substrates were midpoint glass-transition-temperature T<sub>mg</sub>=-3 degree C, transition peak temperature T<sub>wp</sub>=65 degree C by water absorption, and latent-heat =25 J/g average-of-roughness-height R<sub>z</sub>=120nm, the 400nm of the maximum differences of elevation, and saturation water absorption =0.010% of the weight as a result of the same measurement as an example 1.

[0057] When the EL element production process as well as an example 1 was applied to this resin substrate, the yield which it is easy to deform a substrate with heating of a substrate or vacuum evaporation no heat at a spatter or a vacuum evaporation process since the glass transition point is low, and manufactures a uniform EL element was bad.

[0058] Direct current voltage was applied to the manufactured organic EL device, and light was made to emit with the current density of 10 mA/cm<sup>2</sup>. When the initial luminescence condition was observed, 53 island-shape dark spots which do not emit light were observed for 3cm around. Furthermore, continuation luminescence of this component was carried out in 60 degrees C and 90% of ambient atmosphere for 100 hours, and a subsequent dark spot and lowering of brightness were measured. Consequently, breadth and 100 hours after, luminescence was not seen for a dark spot at all on the whole surface.

[0059] (Example 3 of a comparison) As an activity resin substrate, the organic EL device was formed like the example 1 except using the film (the "Dacron film" by Teijin, Ltd.) of polyethylene terephthalate with a thickness of 50 micrometers.

[0060] These substrates were midpoint glass-transition-temperature T<sub>mg</sub>=76 degree C, transition peak temperature T<sub>wp</sub>=74 degree C by water absorption, and latent-heat =14 J/g average-of-roughness-height R<sub>z</sub>=12nm, the 80nm of the maximum differences of elevation, and saturation water absorption =0.125% of the weight as a result of the same measurement as an example 1.

[0061] Direct current voltage was applied to the created organic EL device, and light was made to emit with the current density of 10 mA/cm<sup>2</sup>. When the initial luminescence condition was observed, 35 island-shape dark spots which do not emit light were observed for 3cm around. Furthermore, continuation luminescence of this component was carried out in 60 degrees C and 90% of ambient atmosphere for 100 hours, and a subsequent dark spot and lowering of brightness were measured. Consequently, luminescence was not seen for a dark spot at all breadth and 100 hours after on the whole surface.

[0062] (Example 4 of a comparison) as an activity resin substrate -- a front face -- the organic EL device was formed like the example 1 except using the film ("TEONEKKUSUFIRUMU" by Teijin, Ltd.) of polyethylenenaphthalate resin with a smooth thickness of 50 micrometers.

[0063] These substrates were midpoint glass-transition-temperature T<sub>mg</sub>=118 degree C, transition peak temperature T<sub>wp</sub>=77 degree C by water absorption, and latent-heat =18 J/g average-of-roughness-height R<sub>z</sub>=1.8nm, the 9nm of the maximum differences of elevation, and saturation water absorption =0.209% of the weight as a result of the same measurement as an example 1.

[0064] Direct current voltage was applied to the created organic EL device, and light was made to emit with the current density of 10 mA/cm<sup>2</sup>. When the initial luminescence condition was observed, 46 island-shape dark spots which do not emit light were observed for 3cm around. Furthermore, continuation luminescence of this component was carried out in 60 degrees C and 90% of ambient

atmosphere for 100 hours, and a subsequent dark spot and lowering of brightness were measured. Consequently, luminescence was not seen for a dark spot at all breadth and 100 hours after on the whole surface.

[0065] Separately, for the object of production control, each process (iii) of the above-mentioned examples 1-2 and the examples 1-4 of a comparison, and after (v), the test piece was cut down and content moisture regain was measured by JISK0068 (curl Fischer coulometric titration) from the taken-out component intermediate field. The result is collectively described in the following table 1.

[0066]

[A table 1]

表1: 工程水分含有率 (重量%)

	実施例1	実施例2	比較例1	比較例2	比較例3	比較例4
工程 (iii) 後	0.00001 %以下	0.003 %	0.068 %	0.007 %	0.018 %	0.078 %
工程 (v) 後	0.00001 %以下	0.005	0.158	0.009	0.038	0.198

[0067]

[Effect of the Invention] As mentioned above, according to this invention, the organic EL device excellent in endurance and dependability and its transparent electrode plate are given by using as a substrate the thermoplastics substrate which specified smoothness, absorptivity, and a heat characteristic strictly.

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[Translation done.]

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ABSTRACT:

PROBLEM TO BE SOLVED: To obtain an organic EL element with good durability and high reliability by preventing generation of a defect peculiar to organic EL element, such as generation of a dark spot.

SOLUTION: A metal oxide transparent electrode layer is formed on a thermoplastic substrate. The metal oxide transparent electrode layer with which the thermoplastic resin substrate fills the requirements for the following (a)-(c) is used. (a): surface evenness of not more than 4 nm with a 10-point average roughness Rz based on JIS B0601; (b): low water absorption of

not more than 0.02 W% in saturated water absorption (JIS K7209) by Karl Fischer method (JIS K0068); and (c): the difference  $\Delta T (=T_{mg} - T_{wp})$  between intermediate-point glass transition temperature  $T_{mg}$  and peak endothermic temperature  $T_{wp}$  of thermoplastic resin constituting the substrate, based on JIS K7121 to be  $20^{\circ}\text{C} < \Delta T < 100^{\circ}\text{C}$ .

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